

A Framework for the Analysis of Localized Corrosion at the Proposed Yucca Mountain Repository

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Abstract – *The proposed Yucca Mountain Repository presents a familiar materials performance application that is regularly encountered in energy, transportation and other industries. The widely accepted approach to dealing with materials performance is to identify the performance requirements, to determine the operating conditions to which materials will be exposed and to select materials of construction that perform well in those conditions. A special feature of the proposed Repository is the extremely long time frame of interest, i.e. 10,000's of years and longer. Thus, the time evolution of the environment in contact with waste package surfaces and the time evolution of corrosion damage that may result are of primary interest in the determination of expected performance. An approach is presented to the analysis of localized corrosion during a time period when it is possible for waters from drips and seepage to contact the waste package surfaces, and the analysis is demonstrated for the water chemistry of mixed salt solutions and a set of time-temperature-relative humidity profiles for a hot, mid and cool temperature waste package. Based on the analysis, there are large time periods when localized corrosion can not be supported, and no corrosion damage will occur. Further analysis can then focus on time periods when it is possible for localized corrosion to occur and the determination of the evolution of any corrosion damage.*

I. INTRODUCTION

The determination of materials performance at the proposed Yucca Mountain Repository is amenable to a familiar and effective analytical methodology that is widely accepted in the energy, transportation and other industries. Three components comprise the analysis of materials performance: definition of the performance requirements, determination of the operating conditions to which materials will be exposed and selection of materials of construction that perform well in those conditions. A special feature of the proposed Repository is the extremely long time frame of interest, i.e. 10,000's of years and longer. Thus, the time evolution of the environment in contact with waste package surfaces and the time evolution of corrosion damage that may result are of primary interest in the determination of expected performance.

Corrosion is a primary determinant of waste package performance at the proposed Repository and will control the delay time for radionuclide transport from the waste package. The terrain above the proposed repository and a schematic drawing of waste packages in a drift are shown in Figures 1 and 2, respectively. The waste packages are emplaced on support pallets and held in air. While they will never be fully immersed in water, moisture could form on the metal surfaces from condensation, deliquescence, drips and seepage on waste packages. Depending upon the corrosivity of this moisture, corrosion could occur. This makes corrosion a most

probable and likely degradation process to be analyzed to determine if and when packages will be penetrated and the shape size and distribution of any penetrations.

A framework for the analysis of localized corrosion at the proposed Repository is presented, and the analysis is demonstrated for the water chemistry of mixed salt solutions and a set of time-temperature-relative humidity profiles for hot, mid and cool temperature waste package, i.e. waste packages with a high, medium and low thermal load from the waste [1-3]. The corrosion conditions within the proposed repository are described for five significant time periods from emplacement of waste packages until the repository has returned to ambient conditions after 10,000's of years. An approach is presented to the analysis of localized corrosion during a time period when it is possible for waters from drips and seepage to contact the waste package surfaces.

II. APPROACH TO MATERIALS SELECTION

Since no material is immune to all environmental conditions, the approach is to specify a material with sufficient corrosion resistance over the range of expected environments. The objective is to determine the corrosion behavior over a broad range of environments that cover the expected conditions. Thermal-hydrological-chemical models and experiments determine the water chemistry and temperature ranges of interest [2]. Waters can be grouped into categories of relevance to corrosion behavior, e.g. carbonate waters, sodium-potassium

chloride-nitrate waters, and calcium-magnesium chloride-nitrate waters. The chemical divide processes as illustrated in Figure 3 determine the evolution of water chemistries into the categories of waters shown in Figure 4.

Figure 3 demonstrates the evolutionary paths for multispecies salts starting with a dilute solution that undergoes evaporative concentration [4, 5]. As water evaporates, the solution volume decreases and ionic concentrations increase. The precipitation of calcium carbonate presents the first divide, and a carbonate (no calcium) water path or a calcium (no carbonate) water path is taken depending upon the initial ratio of calcium to carbonate in solution. Further divides are shown for calcium sulfate and magnesium silicate precipitation.

Figure 4 identifies the categories of water chemistries or aqueous solutions that result from the chemical divide analysis. Each category of water is based on the predominant ionic species in the aqueous solution. As dilute waters become more concentrated, three categories of waters are observed: carbonate waters, sulfate waters and chloride – nitrate waters. The chloride – nitrate waters contain sodium, potassium, magnesium and calcium as the predominant cationic species. Upon further concentration, the chloride – nitrate waters evolve to calcium-magnesium rich chloride-nitrate waters. The sulfate waters and carbonate waters can evolve to chloride – nitrate waters with sodium and potassium being the predominant cationic species. An analogous treatment is used to determine the compositions of waters that form starting with dry salts and minerals as water is added. For example, the compositions of waters resulting from deliquescence of multispecies, salts can be determined.

For the various categories of waters, corrosion resistance is determined by long-term exposure of metal specimens and widely accepted electrochemical tests. For example, forward-reverse polarization tests on specimens under fully immersed conditions with severe crevice formers determine the localized corrosion behavior as a function of solution composition, acidity (pH) and temperature. A number of experimental, analytical and computational methods complement and support these studies.

III. CORROSION CONDITIONS AT KEY TIME PERIODS IN REPOSITORY

From a corrosion perspective, five key time periods are defined for any waste package [1, 7]. These periods are defined based on the temperature that the waste packages are expected to experience during the emplacement time. The times for these periods vary from package to package depending on thermal load within the packages and heat transfer in the drift and to the surrounding rock. As explained below, Period IV is a particularly important period for corrosion analysis. Data

for Period IV are presented in Table I for scenarios with mid, hot and cool temperature waste packages. Figure 5 shows the time-temperature-relative humidity trajectories for a mid-temperature waste package.

Period I is prior to closure, and the drifts are ventilated. Corrosion is not of particular concern during this period because the waste packages are relatively cool, and the relative humidity is low. A *thermal barrier* prevents water from dripping or seeping into the drift and falling upon the hot waste package surfaces as long as the drift wall is above the boiling point for waters. For the scenarios described here, the local boiling point for water at Yucca Mountain elevation is used, i.e. 96°C. The thermal barrier develops during the heat up period after closure at the start of Period II and continues through Period III. While the thermal barrier is present, corrosion is of less concern because water can not drip from the rock onto hot metal surfaces. Period V starts when the waste package surface has cooled below the critical temperature for the initiation of localized corrosion of Alloy 22, i.e. taken as 90°C as an exercise for the scenarios presented here.

The start of Period IV is defined as the time when the thermal barrier has dissipated and drips and seepage of water can come from the rock into the drift. For the three scenarios described here, Period IV extends for 625 years (years 750 to 1375) for the mid waste package, 1100 years (years 1900 to 3000) for the hot waste package, and 63 years (years 112 to 175) for the cool waste package. These time periods approach conventional design lives and direct experience with metal behavior over long times. Metal structures are routinely designed for useful lives of 50-100 years, and there are a number of metal artifacts that remain from 1000's of years ago.

During the period IV time period waters from the rock can fall onto hot metal surfaces. Once the packages have cooled below a critical temperature, localized corrosion can no longer initiate. This critical temperature depends upon the corrosion resistance of the waste package outer barrier layer, i.e. Alloy 22 in the base case design. The critical temperature also depends on other conditions in the drift, for example chloride concentration in the water and deposits on surfaces, redox potential of the electrolyte and presence of inhibitors. The evolution of localized corrosion damage once initiated will depend upon the propagation, stifling and arrest processes that prevail with consideration of growth and arrest of localized corrosion that initiated above the critical temperature. While a drip shield is designated as an integral part of the engineered barrier system to prevent any water from directly falling from the rock onto the waste package surface, it is prudent to analyze the corrosion behavior of Alloy 22 under conditions from drips and seepage of water that would occur in absence of the drip shields.

IV. CORROSION ANALYSIS DURING PERIOD IV-COOL DOWN/DRIPPING AND SEEPAGE POSSIBLE

An approach to the analysis during Period IV is illustrated which combines data for the time-temperature-relative humidity trajectories for waste packages along with information on the water chemistry behavior for binary solutions of NaCl and KNO₃. Other salts and salt assemblages can be similarly treated. Figure 6 shows scenarios for three waste packages, and tracks the *time evolution of the aqueous environment* that could be in contact with waste package surfaces [1, 2]. This information is combined with knowledge of the corrosion behavior of Alloy 22 to determine the *time evolution of corrosion damage*. The behavior of chloride-nitrate solutions is important because the relative amounts of chloride and nitrate in solution are found to affect the localized corrosion behavior of Alloy 22. Higher chloride ratios are more aggressive, and higher nitrate ratios are beneficial to corrosion resistance. For example, laboratory experiments find that localized corrosion of Alloy 22 is inhibited in solutions that have a sufficient nitrate to chloride ratio, e.g. NO₃:Cl greater than 0.5 for temperature less than 100°C [6, 8] and NO₃:Cl greater than 0.2 at 90°C [8]. The beneficial nitrate effect can be a function of temperature, and elevated temperatures require more nitrate.

The behavior of a binary mixture of NaCl and KNO₃ as a function of relative humidity and temperature is shown at the top of Figure 6 [9]. For the illustration in Figure 6, the NO₃:Cl ratio of 0.5 is denoted, and other ratios can be analyzed in a similar fashion. The inaccessible region covers the range of temperature-relative humidity conditions that can not be maintained at the atmospheric pressure in the drifts. All binary salt mixtures below the deliquescence relative humidity line are dry (and no corrosion will occur). Pure NaCl deliquesces at nominally 75% Relative Humidity, and the binary mixture deliquesces at nominally 40% Relative Humidity at 125°C and the deliquescence Relative Humidity increases with decreasing temperature. Where aqueous solutions are possible (upper left quadrant), there are constraints on the chemical composition. Below approximately 70% RH, the nitrate to chloride ratio must be greater than 0.5:1. This water chemistry information can then be related to corrosion test data for the behavior of Alloy 22. The temperature-RH trajectories of the mid, hot and cool waste packages described earlier have been plotted on the lower diagram in Figure 6. Key times for Period IV are indicated on the trajectories by diamonds. The significance of this illustration is to demonstrate that the time-temperature-relative humidity behavior is coupled to the water chemistries that can exist on hot

metal surfaces, and the trajectories of aqueous environments can be determined.

The mid range waste package described in Figure 5 begins the cool down period with a temperature of approximately 160°C and relative humidity of 15%, and the trajectory starts at that point on Figure 6. With time, the waste package surface cools and the relative humidity in the drift increases, and the time trajectory tracks from this starting point toward the upper left in the diagram. For this scenario, the thermal barrier, i.e. when the drift wall is above boiling, persists until year 750. At this time, the waste package surface temperature is 101°C and the relative humidity in the drift is 65%. For these conditions, the NO₃:Cl ratio is greater than 0.5 and corrosion tests indicate no localized corrosion of Alloy 22 in these nitrate-chloride solutions. From year 750, the trajectory continues toward the upper left and moves through the water chemistry zones that are noted. The trajectory terminates where the waste package surface is approximately 50°C and relative humidity in the drift is 95%. From Figure 5, it is seen that this is at year 20,000. These calculations can be extended to longer times if desired.

When the waste package surface is dry, there is no corrosion, and there is a critical temperature below which localized corrosion of Alloy 22 will not initiate in waters of a specified composition. For the above scenario, a critical temperature of 90°C is specified, and the waste package surface cools below this temperature in year 1375. The time period over which localized corrosion can initiate is constrained by these two limits, i.e. years 750-1375 for this scenario. Furthermore, the water chemistry of mixed salt solutions is the determinant of temperature-relative humidity conditions within this range. The evolution of localized corrosion damage once initiated then depends upon the propagation, stifling and arrest processes. Based on corrosion performance data for Alloy 22, the conditions that will and will not support localized corrosion are delineated. There are large time periods when localized corrosion can not be supported, and no corrosion damage will occur. The analysis can then further focus on those time periods when localized corrosion could occur. Alloy 22 is susceptible to crevice corrosion especially in chloride rich solutions [10-16]. However, when inhibitors such as nitrate are present in the electrolyte, the localized corrosion susceptibility is suppressed [13, 17-21]. Other factors controlling crevice corrosion include temperature and applied (or redox) potential [22].

V. DECISION-TREE ANALYSIS

An outcome from the analysis described above is that the important time periods when localized corrosion could occur on waste packages are restricted to finite time periods. For the time periods where localized corrosion

can be supported based upon the temperature and possible water chemistries, a decision-tree analysis can be applied to determine the evolution of corrosion damage over time. A decision-tree approach to localized corrosion for the proposed Yucca Mountain repository has been described previously [1, 23]. While the individual steps in these two treatments vary, the overall approach and structure of the decision trees are comparable.

A decision-tree for localized corrosion [1] is presented in Figure 7. Questions considered are:

- Are environments and crevices present to induce localized corrosion? Consider conditions in moist layers of particulate and deposits.
- If localized corrosion initiates, will it persist? Consider corrosion stifling and arrest as the process proceeds.
- What amount of metal penetration occurs?
- What is the size and distribution of corrosion sites?

Based on these considerations, one may determine the evolution of corrosion damage over time. In this analysis, localized corrosion can only proceed when several barriers are overcome, i.e. thermal barrier, capillary barrier and drip shield. Then, water must drip or seep onto the hot, waste package surface and the aqueous environment must be sufficiently corrosive to support crevice corrosion. When these prerequisites are met, then the considerations in the final column to the right are analyzed to determine the evolution of corrosion damage.

VI. SUMMARY

An approach is presented to the analysis of localized corrosion during a time period when it is possible for waters from drips and seepage to contact the waste package surfaces. The analysis is demonstrated for the water chemistry of mixed salt solutions and a set of time-temperature-relative humidity profiles for waste packages. An outcome is that the important time periods when localized corrosion could occur on waste packages are restricted to finite time periods. For these time periods where localized corrosion can be supported based upon the temperature and possible water chemistries, a decision-tree analysis can be applied to determine the evolution of corrosion damage.

Table I. Key Time Period IV data for three scenarios based on a mid, hot and cool thermal load for the waste package.

	Drift Wall 96°C			Waste Package at 90°C
	Year	Waste Package Temp °C	Relative Humidity	Year
Mid WP	750	101	65	1375
Hot WP	1900	99	56	3000
Cool WP	112	102	72	175



Fig. 1. Proposed Yucca Mountain Repository.

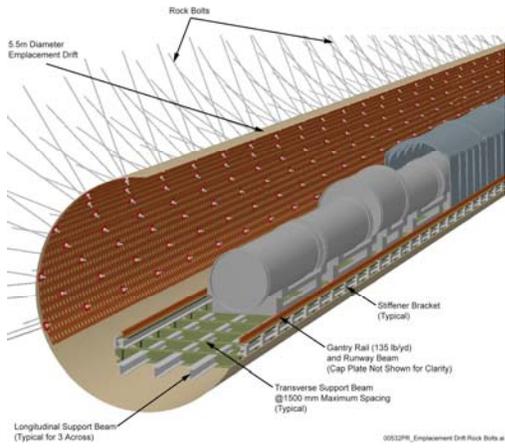


Fig. 2. Waste packages in a drift.

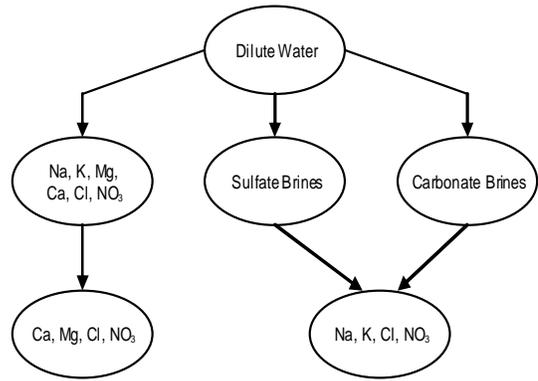


Fig. 4. Categories of aqueous solutions.

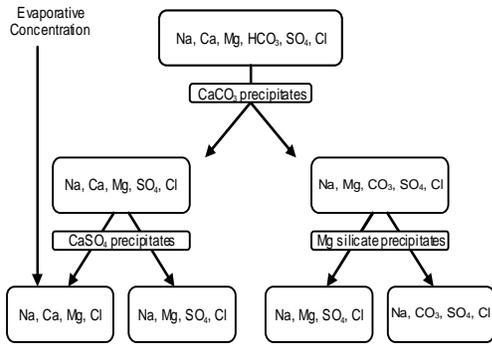


Fig. 3. Chemical divide processes.

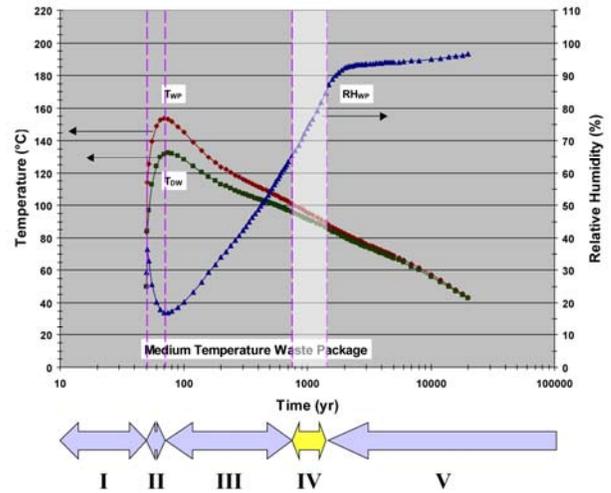


Fig. 5. The temperature and relative humidity trajectories for a medium temperature waste package and five key time periods on a logarithmic time scale. During Period I (Preclosure) the drifts are ventilated, temperature is near ambient and relative humidity is low.

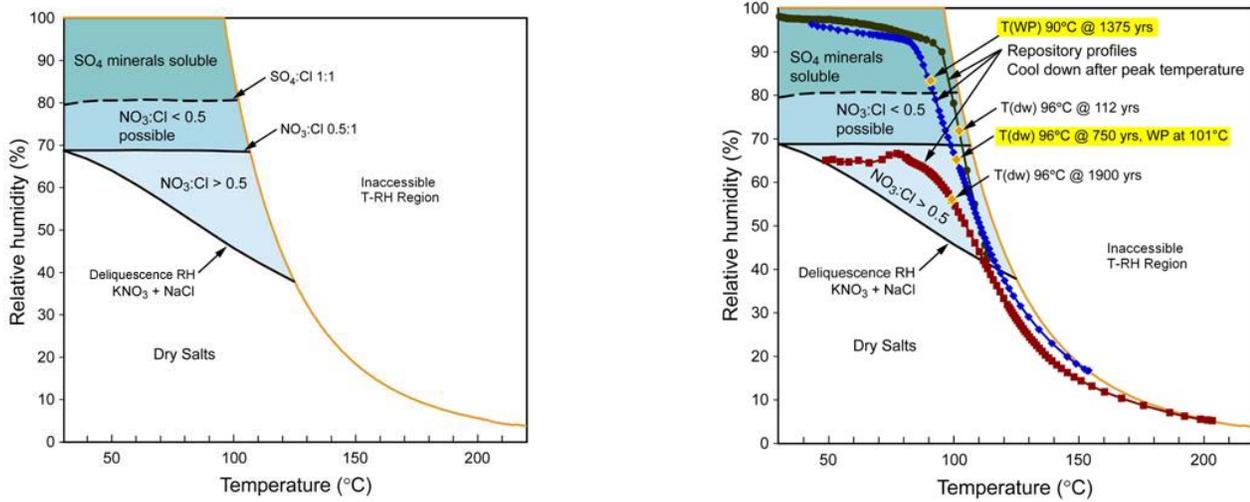


Fig. 6. The water chemistry (right) of a binary mixture of NaCl and KNO₃ and the temperature-RH trajectories (left) of the mid, hot and cool waste packages.

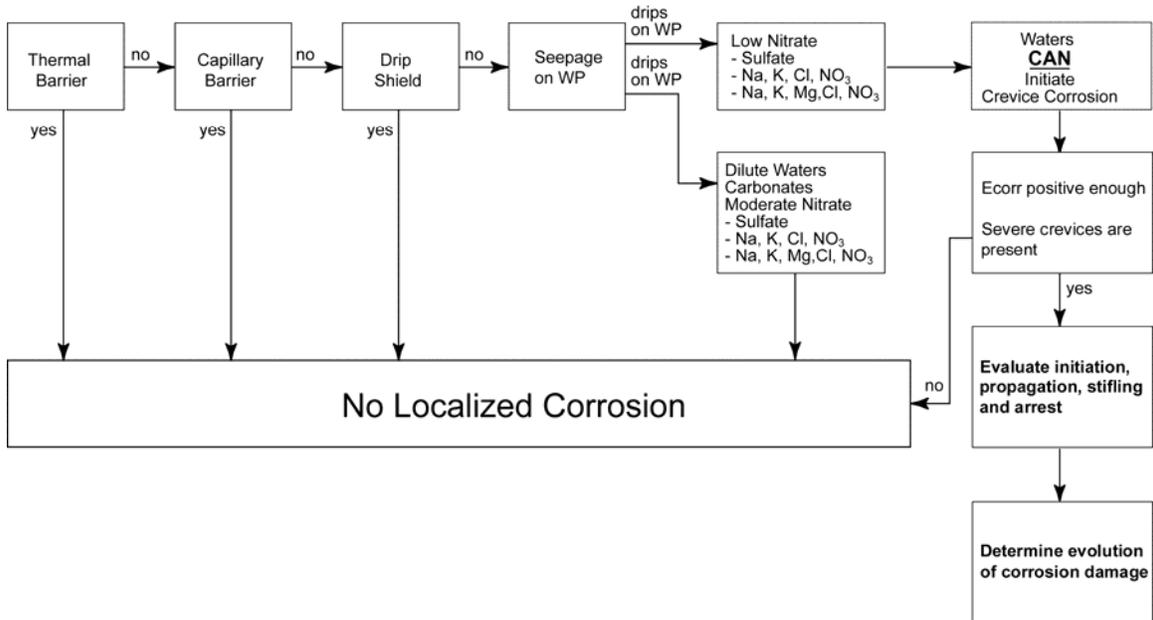


Fig. 7. A decision-tree diagram for localized corrosion.

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